

Thermal Conductivity Minimum: A New Water Anomaly

Pradeep Kumar and H. Eugene Stanley

Center for Polymer Studies and Department of Physics,

Boston University, Boston, MA 02215 USA

Many anomalies of water have been discovered. Some concern the static thermodynamic properties of water, such as the increase of compressibility and specific heat upon decreasing the temperature. Others concern the dynamic properties, such as the breakdown of the Stokes-Einstein relation in supercooled water ¹ and the non-Arrhenius to Arrhenius dynamic crossover ^{2,3}.

The thermal conductivity Λ is the proportionality constant between heat flux and temperature gradient that causes the flux. Upon decreasing temperature below its maximum at 400 K ^{4,5}, Λ decreases. However no data have been reported below ≈ 268 K. Using molecular dynamics computer simulations of water down to $T = 220$ K, we find the surprising result that the Λ displays a minimum at lower temperatures, $T_{\min} = 250$ K. Our simulations are for the TIP5P model of water which is known to reproduce experimental data well at ambient pressures ^{6,7}.

We first perform equilibrium simulations at atmospheric pressure for temperatures from 300 K down to 220 K in the NPT ensemble using the Berendsen thermostat and barostat with

a time step of 1 fs. We then run the equilibrated configurations at different T in the NVE and NVT ensembles to generate the results from which we calculate Λ . To calculate Λ , we use two different methods: (i) the Green-Kubo relation between Λ and the energy current correlation function ⁸, and (ii) the Müller-Plathe algorithm ⁹. Our values for Λ obtained from both methods differ from each other by less than 15%.

Figure 1(a) shows that Λ decreases with decreasing T , reaching a minimum at $T_{\min} \approx 250$ K, and increases upon further decrease in T . A clue to the possible interpretation of this surprising result is provided by the observation that the temperature at which Λ displays a *minimum* is the same temperature at which the specific heat C_P displays a *maximum* [see Fig. 1(b)].

In fact, a maximum in C_P occurs upon crossing the locus of maximum correlation length, the Widom line $T_W(P)$ ³, emanating from the hypothesized liquid-liquid critical point ¹⁰. Below $T_W(P)$, water becomes locally more tetrahedral ¹¹, and the local structure of liquid water below $T_W(P)$ more resembles ice I_h . Hence Λ should increase with further decrease in temperature below $T_W(P)$.

Finally we calculate the thermal diffusivity D_T , related to ρ , Λ and C_P as

$$D_T = \frac{\Lambda}{\rho C_P}. \quad (1)$$

Figure 1(c) show that D_T decreases very slowly upon decreasing T and rises sharply upon further decreasing T below the temperature of maximum C_P .

In summary, we report a new anomaly of water, a minimum in the thermal conductivity. Our

findings are of special interest since they support the presence of a liquid-liquid phase transition in water¹⁰.

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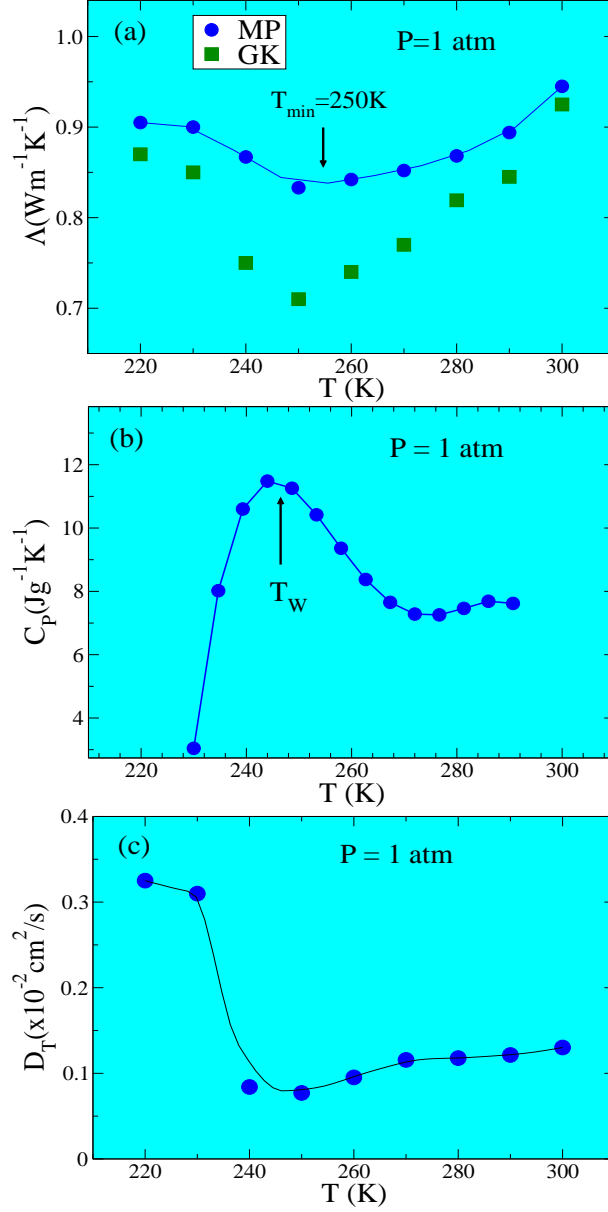


Figure 1: (a) Temperature dependence of the thermal conductivity Λ of TIP5P water, showing a minimum at $T_{\min} \approx 250 \text{ K}$. Values of Λ obtained from the Müller-Plathe algorithm are shown as filled circles and Λ obtained via the Green-Kubo relation are shown as filled squares. (b) Temperature dependence of the specific heat C_P showing a maximum at $T_W \approx 250 \text{ K}$. (c) Temperature dependence of the thermal diffusivity $D_T = \Lambda/\rho C_P$, showing a sharp increase below $T_W(P)$.

Acknowledgements We thank S.-H. Chen for helpful comments and the NSF Chemistry Program for support.

Competing Interests The authors declare that they have no competing financial interests.

Correspondence Correspondence and requests for materials should be addressed to Pradeep Kumar (email: pradeep@buphy.bu.edu).